

**METHOD FOR UPGRADING LUBE OIL
BOILING RANGE FEEDSTREAMS BY
TREATMENT WITH A SULFURIC ACID SOLUTION**

FIELD OF THE INVENTION

[0001] The instant invention relates to a method for upgrading nitrogen-containing hydrocarbon streams. More particularly, the present invention relates to an improved hydroprocessing method for lube boiling range feedstreams involving contacting the lube oil boiling range feedstream with an acidic solution to remove heterocyclic nitrogen-containing compounds prior to hydroprocessing.

BACKGROUND OF THE INVENTION

[0002] Currently, there exists a need to reduce the heterocyclic nitrogen content of feedstreams used in the lube oil processes because heterocyclic nitrogen-containing compounds, especially basic heterocyclic nitrogen-containing compounds, contained in lube oil boiling range feedstreams act as competitive inhibitors on the catalytic sites of catalysts. These nitrogen-containing compounds are indigenous to crude oils, and are typically concentrated in the higher boiling fractions, such as lube oil fractions. The presence of these heterocyclic nitrogen-containing compounds typically prevents lube oil hydroprocesses from operating as effectively and/or efficiently as possible. For example, the presence of these heterocyclic nitrogen-containing compounds in lube oil boiling range feedstreams used in hydrocracking operations ~~requires that the hydrocracking~~ be performed at high temperatures that impart a higher degree of over-cracking and lube oil boiling range yield loss when compared to hydrocracking processes that operate at a lower temperature.

[0003] Also, the removal of nitrogen species from lube oil boiling range feedstreams allow cracking operations to operate more efficiently because

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these heterocyclic nitrogen-containing compounds, especially basic heterocyclic nitrogen-containing compounds, act as competitive inhibitors on the acidic cracking sites of cracking catalysts. Thus, many methods for reducing the nitrogen content in feedstreams have been proposed.

[0004] For example, United States Statutory Invention Registration H1368, Fraytet, teaches the use of concentrated sulfuric acid, i.e. at least 95 wt.% sulfuric acid, to treat straight run jet fuel boiling range streams. The process requires that the sulfuric acid-containing stream be dispersed in the jet fuel in the form of droplets smaller than about 300 microns. The Fraytet process discloses that 90% or more of the nitrogen can be removed from the jet fuel boiling range stream.

[0005] United States Patent Number 4,392,948, Debande, teaches the use of acidic treatments for straight run distillates boiling in the range of 150°C to about 290°C. The acidic solution used in Debande has an acid concentration from about 0.01 to about 2.5 vol.%. This acid is contacted with the straight run distillate feedstream for a short period of time, i.e. not to exceed two seconds.

[0006] However, there still exists a need in the art for a more effective nitrogen removal method to be used in hydroprocessing schemes for lube oil boiling range feedstreams because with their removal, lube hydroprocessing operations could be improved.

SUMMARY OF THE INVENTION

[0007] One embodiment of the instant invention is directed at an improved method for hydroprocessing a nitrogen-containing lube oil boiling range feedstream. The method comprises:

- a) providing a sulfuric acid solution having a sulfuric acid concentration of at least about 75 vol.%, based on the sulfuric acid solution;
- b) contacting a nitrogen-containing lube oil boiling range feedstream with the sulfuric acid solution under conditions effective at removing at least about 60 wt.% of the nitrogen compounds contained in said lube oil boiling range feedstream, wherein the volumetric treat rate of the sulfuric acid solution is greater than about 0.5 vol.%, based on the lube oil boiling range feedstream thereby producing at least a mixture comprising a lube oil boiling range effluent and a used sulfuric acid solution; and
- c) processing said lube oil boiling effluent by at least one process selected from, solvent extraction, hydrocracking, hydrotreating, hydrodewaxing, and hydrofinishing thereby producing a lube oil boiling range product.

[0008] In preferred embodiments of the instant invention the sulfuric acid solution is a spent sulfuric acid solution obtained from an alkylation process unit.

[0009] In one embodiment, the lube oil boiling range product is hydrotreated to produce a hydrotreated lube oil boiling range product that is subsequently processed by a process selected from solvent dewaxing, solvent extraction, hydrodewaxing, hydrocracking, hydrofinishing, and mixtures thereof.

[0010] In another embodiment, the improved method further comprises contacting the lube oil boiling range product with an effective amount of an acid reducing material selected from caustic and water under conditions effective at reducing the total acid number of said lube oil boiling range product prior to step(c).

BRIEF DESCRIPTION OF THE FIGURE

[0011] The Figure illustrates that the boiling range conversion of the acid treated lube oil boiling range feedstock takes place with reactor temperature requirements that are 16-20°C lower than that for the same boiling range conversion of the base, untreated feedstock.

DETAILED DESCRIPTION OF THE INSTANT INVENTION

[0012] Catalytic processes are typically impeded by the presence of nitrogen, among other things. The nitrogen, which is usually present as heterocyclic molecules, act as competitive inhibitors of catalytic sites. In lubes processing, the nitrogen-containing heterocyclic molecules force refiners to operate hydrocracking processes at temperatures higher than desired. This increased operating temperature increases the relative amount of over-cracking and lube oil boiling range yield loss when compared to a process operated at lower temperatures. Thus, by reducing the content of nitrogen-containing heterocyclic species in a feedstream, hydrocracking processes can be operated at lower temperatures that favor more selective cracking thereby increasing both lube oil product yield and viscosity index ("VI") and extending the useful life of catalysts. The removal of heterocyclic nitrogen species also permits the practitioner of hydrocracking processes to utilize hydrogen pressures lower

than processes utilizing feedstreams having higher nitrogen concentrations. The reduction in nitrogen-containing heterocyclic molecules similarly benefits other lube oil processes such as, for example, hydrodewaxing, hydrotreating and hydrofinishing.

[0013] Therefore, the instant invention is directed at an improved method for hydroprocessing a nitrogen-containing lube oil boiling range feedstream. In the instant invention, a nitrogen-containing lube oil boiling range feedstream is contacted with a sulfuric acid solution, thus reducing the nitrogen content of the lube oil boiling range feedstream by at least 60 wt.%. The contacting of the nitrogen-containing lube oil boiling range feedstream with the sulfuric acid solution produces at least a lube oil boiling range effluent. The lube oil boiling range effluent so produced is subsequently processed by at least one process selected from hydrocracking, hydrotreating, hydrodewaxing, hydrofinishing, and any mixtures thereof. These processes are sometimes referred to herein as hydroprocessing. The lube oil boiling range effluent may also be subsequently processed by solvent extraction.

[0014] Lube oil boiling range feedstreams suitable for treatment in the present methods include any conventional lube oil boiling range feedstreams used in lube oil processing. Such feedstreams typically include wax-containing feedstreams such as feeds derived from crude oils, shale oils and tar sands as well as synthetic feeds such as those derived from the Fischer-Tropsch process. Typical wax-containing feedstocks for the preparation of lubricating base oils have initial boiling points of about 315° C or higher, and include feeds such as reduced crudes, hydrocrackates, extracts, hydrotreated oils, atmospheric gas oils, vacuum gas oils, coker gas oils, atmospheric and vacuum resids,

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deasphalted oils, slack waxes and Fischer-Tropsch wax. Such feeds may be derived from distillation towers (atmospheric and vacuum), hydrocrackers, hydrotreaters and solvent extraction units, and may have wax contents of up to 50% or more. Preferred lube oil boiling range feedstreams boil above about 650°F (343°C).

[0015] The lube oil boiling range feedstreams suitable for treatment by the present methods contain, among other things, heterocyclic nitrogen-containing compounds. The total nitrogen content of such streams is typically greater than about 100 wppm, more typically it ranges from about 1000wppm to about 2000wppm. Thus, these streams are sometimes referred to herein as nitrogen-containing lube oil boiling range feedstreams. The nitrogen compounds appear as both basic and non-basic nitrogen species. Non-limiting examples of basic nitrogen species may include quinolines and substituted quinolines, and non-limiting examples of non-basic nitrogen species may include carbazoles and substituted carbazoles.

[0016] In practicing the embodiments of the instant invention, the above-defined lube oil boiling range feedstreams are intimately contacted with a sulfuric acid solution to remove at least about 60 vol.% of the nitrogen species, both basic and non-basic. The sulfuric acid solution used herein contains at least about 75 wt.% sulfuric acid, based on the sulfuric acid solution, preferably greater than about 80 wt.%, more preferably about 85 wt.% to about 93 wt.%. The sulfuric acid solution may be obtained through any means known. However, in one embodiment the sulfuric acid solution is the spent sulfuric acid obtained or recycled from an alkylation process unit having a sulfuric acid concentration within the above-defined ranges.

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[0017] A typical alkylation process involves combining an olefinic hydrocarbon feedstream containing C₄ olefins with isobutane to produce a hydrocarbonaceous mixture. This hydrocarbonaceous mixture is subsequently contacted with sulfuric acid. The sulfuric acid used for contacting the hydrocarbonaceous mixture is typically reagent grade sulfuric acid having an acid concentration of at least about 95 wt.%. Preferably the sulfuric acid has a sulfuric acid concentration of greater than about 95 wt.%. The hydrocarbonaceous mixture is contacted with the sulfuric acid under conditions effective at producing at least an alkylate and a sulfuric acid solution. The sulfuric acid solution so produced comprises at least about 75 wt.% sulfuric acid, based on the sulfuric acid solution, preferably greater than about 80 wt.% sulfuric acid, more preferably about 85 vol.% to about 93 wt.% sulfuric acid. The sulfuric acid solution also typically contains about 0.5 to about 5 wt.% water, with the remaining balance being acid suspended hydrocarbons. It is more preferred that the effective conditions be selected such that the sulfuric acid solution so produced comprises between about 82 and 92 wt.% sulfuric acid, about 1 to about 4 wt.% water, with the remaining balance being suspended hydrocarbons. However, it is most preferred that the effective conditions be selected such that the sulfuric acid solution so produced comprises between about 85 and 93 wt.% sulfuric acid, about 1.5 to about 4 wt.% water, with the remaining balance being suspended hydrocarbons.

[0018] It should be noted that it is within the scope of the present invention to dilute the sulfuric acid obtained from the alkylation unit, or otherwise, with a suitable diluent, preferably water, in order to provide a sulfuric acid solution having the above-described concentration of sulfuric acid, i.e. at least about 75

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wt.% sulfuric acid, based on the sulfuric acid solution, preferably greater than about 80 wt.%, more preferably about 85 wt.% to about 93 wt.%. In order to determine the sulfuric acid concentration once the diluent has been added to the sulfuric acid solution, the sulfuric acid content and water content are measured by standard analytical techniques. The equivalent acid strength once a diluent has been added or if suspended hydrocarbons are present can then be calculated with the following formula: $\text{equivalent wt\% sulfuric acid} = \text{wt\% sulfuric acid} / (\text{wt\% sulfuric acid} + \text{wt\% water})$.

[0019] As discussed above, the lube oil boiling range feedstream is contacted with the sulfuric acid solution at an acid volumetric treat rate of greater than about 0.5 vol.%, based on the lube oil boiling range feedstream, preferably greater than about 1.0 vol.% more preferably about 1.0 vol.% to about 5.0 vol.%. The contacting can be achieved by any method known. Non-limiting examples of suitable contacting methods include passing the sulfuric acid solution and the lube oil boiling range feedstream through a mixing valve, mixing the sulfuric acid solution and the lube oil boiling range feedstream in a mixing tank or vessel, and, passing the sulfuric acid solution and the lube oil boiling range feedstream through a packed bed of inert particles, and other comparable methods. In a preferred embodiment, a mixing tank or mixing valve is used to contact the lube oil boiling range feedstream and the sulfuric acid solution.

[0020] The contacting of the lube oil boiling range feedstream with the sulfuric acid solution occurs under effective conditions. By effective conditions, it is to be considered those conditions that allow the present method

to achieve a reduction of nitrogen of at least about 60 wt.%, preferably greater than about 75 wt.%, more preferably greater than 80 wt.%.

[0021] The contacting of the lube oil boiling range feedstream with the sulfuric acid solution produces at least a mixture comprising a lube oil boiling range effluent and a used sulfuric acid solution. The mixture is preferably separated into a lube oil boiling range effluent and the sulfuric acid solution. The used sulfuric acid solution, which now contains the removed nitrogen species, and the lube oil boiling range effluent can be separated by any means known to be effective at separating an acid from a hydrocarbon stream. Non-limiting examples of suitable separation methods include gravity settling, electric field induced settling, centrifugation, microwave induced settling and settling enhanced with coalescing surfaces. However, it is preferred that the lube oil boiling range effluent and the sulfuric acid solution be separated, or allowed to separate, into layers in a separation device such as a settling tank or drum, coalescer, electrostatic precipitator, centrifuge, or other similar device.

[0022] The lube oil boiling range effluent thus obtained by the present method will contain substantially less nitrogen, both basic and non-basic, than the initial lube oil boiling range feedstream. By substantially less, it is meant that the nitrogen content of the lube oil boiling range feedstream is reduced by at least about 60 wt.%, preferably greater than about 75 wt.%, more preferably at least 80 wt.%. This will typically result in a lube oil boiling range effluent having a nitrogen level of less than about 800 wppm, preferably less than about 500wppm, more preferably less than about 400 wppm, and most preferably less than about 200 wppm.

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[0023] The lube oil boiling range effluent is typically collected from or withdrawn from the separation device and passed to a suitable lube oil process such as, for example, hydrodewaxing, hydrocracking hydrotreating, hydrofinishing, solvent extraction, and mixtures thereof. In this embodiment, any suitable hydrodewaxing, hydrocracking, hydrotreating, or hydrofinishing catalyst can be used under any conditions effective at achieving the results sought by the practitioner, i.e. converting a certain percentage of the feed, i.e. the lube oil boiling range product, in hydrocracking operations, removing a certain amount of sulfur impurities in hydrotreating operations, etc. In one embodiment, the lube oil boiling range effluent is hydrotreated to produce a hydrotreated lube oil boiling range product that is subsequently processed by a process selected from solvent dewaxing, solvent extraction, hydrodewaxing, hydrocracking, hydrofinishing, and mixtures thereof.

[0024] The sulfuric acid treatment, however, also results in a lube oil boiling range effluent that is typically more acidic than the lube oil boiling range feedstream. The measure of acidity referenced herein is the total acid number ("TAN") of the feedstream or effluent. The TAN can be described as a quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point, as measured by ASTM method D-664. A more acidic feed can have a detrimental effect on processing equipment, etc because of its corrosive nature. Thus, one embodiment of the instant invention involves contacting the lube oil boiling range effluent, prior to processing said lube oil boiling effluent by a process selected from solvent extraction, hydrocracking, hydrotreating, hydrodewaxing, hydrofinishing, and mixtures thereof with an effective amount of a material selected from caustic and water, preferably water. By an effective amount of

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material, it is meant that amount of material that reduces the TAN of the lube oil boiling range effluent. The lube oil boiling range effluent is contacted with the caustic or water under effective conditions. By effective conditions, it is meant those conditions, that when selected, allow for the reduction of the TAN of the lube oil boiling range effluent. Preferably the effective amount of material and the effective conditions are selected such that the TAN of the lube oil boiling range effluent is equal that of the lube oil boiling range feedstream. More preferably the effective amount of material and the effective conditions are selected such that the TAN of the lube oil boiling range effluent is lower than that of the lube oil boiling range feedstream.

[0025] The above description is directed at several embodiments of the present invention. Those skilled in the art will recognize that other embodiments that are equally effective could be devised for carrying out the spirit of this invention.

[0026] The following examples will illustrate the improved effectiveness of the present invention, but is not meant to limit the present invention in any fashion.

EXAMPLES**EXAMPLE 1**

[0027] A lube oil boiling range feedstock to a lubricant hydrocracker was chosen for a comparative hydrocracking study with an acid treated version of said feed. The lube oil boiling range feedstream was composed of a blend of heavy coker gas oil, heavy vacuum gas oil, and light vacuum gas oil, nominally in a 6:2:1 ratio, respectively. The feed had a nitrogen concentration of 1761 wppm, a sulfur concentration of 26540 wppm, and a total aromatics concentration of 1576 mmol/kg. The experiment was designed to show the impact of acid treating on catalyst performance and product quality in a pilot scale unit.

[0028] 20-gallons of the lube oil boiling range feedstock was treated at a temperature of 150°F with a sulfuric acid solution having a sulfuric acid concentration of 95 wt.%. The lube oil boiling range feedstock was contacted with the sulfuric acid solution at a treat rate of 3 vol.% by continuous mixing via a static mixer followed by centrifugal separation of the sulfuric acid solution using a Podbielniak Centrifugal Extractor. The acid treated lube oil boiling range feedstock was then subjected to a water wash at 150°F by mixing/separating in the same fashion and apparatus with a 10 vol% treat rate of water.

[0029] A loss of 4.7 wt% of lube oil boiling range feedstock to the sulfuric acid stream was calculated by elemental analysis of the used acid stream. In conjunction with this small material loss, the treated feed exhibited significantly lowered nitrogen content (measured by ANTEK), reduction in sulfur content (measured by X-ray fluorescence spectrometry), and reduction in

total aromatic content (measured by UV spectrometry). The results of the acid treatment, i.e. the nitrogen, sulfur, and total aromatics concentration of the acid treated and water washed lube oil boiling range feedstock, are summarized in Table 1, below.

| TABLE 1 | | | | |
|-----------------|-------------------------|----------------|--------------|---------------------------|
| Feed Type | Acid Treat Rate (vol.%) | Nitrogen (ppm) | Sulfur (ppm) | Total Aromatics (mmol/Kg) |
| Base, untreated | 0 | 1761 | 26540 | 1576 |
| Acid, treated | 3 | 578 | 24950 | 1510 |

EXAMPLE 2

[0030] The base feed and the acid treated feed described in Example 1 were then directly compared in a pilot unit operated under hydrocracking conditions. The pilot unit was operated at 1700 psig H₂ pressure with 6750 scf/bbl H₂ treat gas. The pilot unit was loaded with 262 cc of commercially available supported Ni/Mo hydrocracking catalysts, which were sulfided in situ. The feedstocks were processed at 0.6 hr⁻¹ LHSV. To achieve a comparison between the two feedstocks, each was processed at a temperature range that spanned 50 - 80 wt% conversion of material out of the 370°C+ typical lubricant boiling range, with a 70 wt% conversion being typically required to produce desired lubricant product quality. The conversion versus reactor temperature profile is shown in the Figure, herein.

[0031] The Figure illustrates that the boiling range conversion of the acid treated lube oil boiling range feedstock takes place with reactor temperature requirements that are 16-20°C lower than that for the same boiling range conversion of the base, untreated feedstock.

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[0032] While not wishing to be limited by theory, the inventors hereof believe the reduction in operating temperature may be taken advantage of in at least three ways. The first would be to simply allow a modest improvement in product quality as shown in Example 3, below. The second would be to extend catalyst lifetime by lowering operational temperature. Hydrocracking catalyst temperature requirements increase gradually with aging until an end of cycle temperature limit is reached, so lowering operational temperature requirements to make the desired product should extend the catalyst lifetime. The third would be to increase unit throughput, effectively expanding the amount of feedstock processed. In hydrocracking, increased throughput requires increased reactor temperature to maintain a constant conversion level (to meet product quality). Because the acid treated case requires an operating temperature that is 17°C lower while still meeting conversion requirements, the feed rate could be increased substantially. The increased feed rate would require increased reactor temperature to meet required conversion levels, but the 17°C window should allow for the temperature increase and still allow the temperature to be in a normal operating range.

EXAMPLE 3

[0033] To demonstrate the benefits achieved by sulfuric acid treatment on processes such as dewaxing, which occur subsequent or downstream of the hydrocracking operation, the 370°C+ fraction described in Example 2 above was subjected to solvent dewaxing. It should be noted that acid treating does not directly improve solvent dewaxing, a physical separation process. However, by improving the hydrocracking operation from which the lube oil boiling range feedstream subjected to solvent dewaxing is obtained, a product from solvent dewaxing operation downstream from the hydrocracker can also

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be impacted by impacting product characteristics. Thus, the solvent dewaxing was done to illustrate product quality benefits on a basestock produced from a hydrocracking operation involving sulfuric acid treatment prior to hydrocracking. Therefore, this example is intended to demonstrate benefits to processes downstream from a hydrocracking operation employing a sulfuric acid treatment process thereby illustrating the benefits of the sulfuric acid treatment discussed above for hydrocracking. It should further be noted that the examination of a lube oil basestock obtained from solvent dewaxing provides a standard measure of comparison, since only minimal properties of the hydrocrackate itself are typically monitored.

[0034] The dewaxing was conducted under standard laboratory solvent dewaxing conditions using methyl isobutyl ketone dilution with chilling and filtration to produce dewaxed oil with a -18°C pour point. The conditions included weighing approximately 125g of a waxy $370^{\circ}\text{C}+$ lube oil hydrocrackate from Example 2 and approximately 250g of MIBK and thence adding these into a flask and heating to miscibility to form a slurry. The slurry was weighed and placed in a chilled isopropyl alcohol/dry ice bath, where it was stirred and chilled to the target dewaxing temperature of -18°C . The chilled slurry was vacuum-filtered through filter paper in a jacketed Buchner funnel cooled by a circulating refrigeration bath to maintain target dewaxing temperature. The wax cake and dewaxed filtrate were retained, the solvent was removed from each by stripping in a rotary evaporator, and the stripped wax and dewaxed oil were weighed. The wax content was calculated directly, the VI of the dewaxed oil was measured with a Houllion automatic viscometer, and the dewaxed oil saturates were measured by physical chromatographic separation. The results of this Example are summarized in Table 2, below.

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| TABLE 2 | | | | | |
|-----------------|--------------------------------|--|----------------------------|---|--|
| Feed Type | 370°C+ conversion (wt.%) | Reactor Temperature Required (°C) | -18°C Dewaxed Oil VI | Wax Content (-18°C dewaxing, wt.%) | -18°C Dewaxed Oil Saturates (wt.%) |
| Base, untreated | 70 | 382 | 106 | 15.7 | 92 |
| Acid, treated | 70 | 365 | 107 | 16.7 | 97 |

[0035] These examples provide evidence that a typical hydrocracking feedstock can be mildly treated with sulfuric acid to significantly reduce its nitrogen content. Due to the lowered nitrogen level, hydrocracking the acid treated feedstock required reduced catalyst operating temperatures and produced an improved product over hydrocracking a non-treated feedstock, as evidenced by the basestock properties.